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FORMING ORGANIZATION REPORT NUMBER(S)

1b. RESTRICTIVE MARKINGS

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5. MONITORING ORGANIZATION REPORT NUMBER(S)

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University of North Carolina6b. OFFICE SYMBOL
(If applicable)

7a. NAME OF MONITORING ORGANIZATION

Office of Naval Research

6c. ADDRESS (City, State, and ZIP Code)

Campus Box 3290
Chapel Hill, NC 27599-3290

7b. ADDRESS (City, State, and ZIP Code)

Department of the Navy
Arlington, VA 222178a. NAME OF FUNDING/SPONSORING
ORGANIZATION8b. OFFICE SYMBOL
(If applicable)

9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER

N0014-89-J-1734

8c. ADDRESS (City, State, and ZIP Code)

10. SOURCE OF FUNDING NUMBERS

PROGRAM
ELEMENT NO.PROJECT
NO.TASK
NO.WORK UNIT
ACCESSION NO.11. TITLE (Include Security Classification) UNCLASSIFIED: Magnetic and Electrical Properties of
Sandwich-Like Lanthanide Phthalocyanines

12. PERSONAL AUTHOR(S)

Juan Padilla and William E. Hatfield

13a. TYPE OF REPORT

Technical Report

13b. TIME COVERED

FROM TO

14. DATE OF REPORT (Year, Month, Day)

May 8, 1989

15. PAGE COUNT

10

16. SUPPLEMENTARY NOTATION

Technical Report No. 34

17. COSATI CODES

FIELD

GROUP

SUB-GROUP

18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)

electrical conductivity, magnetic susceptibility, lutetium,
phthalocyanines, electron paramagnetic resonance,
semiconductors

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

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D.C. conductivity measurements on pellets in the temperature range 20 to 300 K yielded values on the order of 10^{-5} to 10^{-4} S cm⁻¹ for the undoped phthalocyanines, and 10^{-2} to 10^{-1} S cm⁻¹ for the doped ones. The conductivity behavior may be explained in terms of the variable-range hopping mechanism for heavily-doped semiconductors.

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Contract N0014-89-J-1734

R&T Code 4135007---05

TECHNICAL REPORT NO. 34

Magnetic and Electrical Properties of
Sandwich-Like Lanthanide Phthalocyanines

by

Juan Padilla and William E. Hatfield

Prepared for Publication in

Synthetic Metals

The Department of Chemistry, The University of North
Carclina at Chapel Hill, North Carolina, 27599, U.S.A.

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MAGNETIC AND ELECTRICAL PROPERTIES OF SANDWICH-LIKE LANTHANIDE
PHTHALOCYANINES

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ABSTRACT

Rare-earth phthalocyanine sandwich compounds and their iodine analogues have been synthesized. Single crystals were obtained by electrochemical means, and magnetic susceptibility measurements on the polycrystalline samples follow the Curie-Weiss law. Room temperature and 77 K EPR spectra at X-band for undoped lutetium phthalocyanine indicate the presence of a free-radical phthalocyanine unit. Doped complexes also show a narrow signal with a g-value of 2.00.

D.C. conductivity measurements on pellets in the temperature range 20 to 300 K yielded values on the order of 10^{-5} to 10^{-7} S cm^{-1} for the undoped phthalocyanines, and 10^{-2} to 10^{-4} S cm^{-1} for the doped ones. The conductivity behavior may be explained in terms of the variable-range hopping mechanism for heavily-doped semiconductors.

INTRODUCTION

Since the lanthanide phthalocyanines were synthesized for the first time in 1965 [1], there has been a growing interest in this kind of compounds. They have a sandwich-like structure with the lanthanide ion located between the two macrocyclic phthalocyanine units. Like their transition metal analogues, after partial

oxidation with iodine, they show a substantial increase in the electrical conductivity. Most of the studies have been done on neodymium phthalocyanine [2-7]. We have extended the measurements to praseodymium, neodymium, gadolinium, holmium, erbium, and lutetium phthalocyanines, from 20 to 300 K, using D.C. techniques. The magnetic properties of both undoped and doped phthalocyanines are also described.

EXPERIMENTAL

Synthesis

The synthesis and purification of the lanthanide phthalocyanines was carried out in a similar way to the one described previously [1]. The iodine doped materials were prepared by mixing the lanthanide phthalocyanine powders with an excess of iodine dissolved in benzene, and subsequent stirring for two days at room temperature. The products were isolated by filtration, then washed with benzene, and dried for several hours under vacuum. In the case of erbium, toluene was substituted for benzene. Single crystals were also obtained by mixing of the appropriate lanthanide phthalocyanine and an excess of tetrabutylammonium iodide dissolved in freshly distilled DMF, and electrocrystallized using a constant current for three days.

Conductivity measurements

Four-probe D.C. electrical conductivity measurements were collected on pressed pellets 1.3 cm in diameter, and approximately 0.1 cm in thickness over the temperature range 20 to 300 K. The sample pellets were mounted on a ceramic insulating material.

To assure good contacts and eliminate interface resistance between the probes and the pellet surface, the samples were spotted with conductive silver paste. The electrical connection was accomplished with four equally spaced (1.1 mm) spring-loaded electrodes.

The samples were routinely screened at room temperature for ohmic behavior and low contact resistance. Typically, a current of 50×10^{-6} Amps was used.



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Magnetic measurements

Magnetic susceptibilities were measured from 4.2 to 77 K with a PAR model 155 vibrating sample magnetometer. Samples were enclosed in lucite holders. The measurements were performed at 10 kG. The magnetic susceptibilities from 77 K to room temperature were measured with a Faraday balance. Diamagnetic corrections were calculated from Pascal's constants and the tabulated constitutive corrections constants [8,9]. The instruments were calibrated with $\text{HgCo}(\text{SCN})_4$.

EPR experiments were carried out on a Varian E-109 X-band spectrometer. The field was calibrated with DPPH ($g = 2.0036$).

RESULTS AND DISCUSSION

Electrical conductivities

The results of the D.C. conductivity measurements at room temperature for both undoped and doped lanthanide phthalocyanines are shown in Table 1.

TABLE 1

D.C. electrical conductivities σ (S cm^{-1}) at room temperature

Compound	σ	Compound	σ
$\text{Pr}(\text{Pc})_2$	$< 10^{-8}$	$\text{Pr}(\text{Pc})_2\text{Ix}$	4.7×10^{-3}
$\text{Nd}(\text{Pc})_2$	7.6×10^{-8}	$\text{Nd}(\text{Pc})_2\text{Ix}$	6.5×10^{-2}
$\text{Gd}(\text{Pc})_2$	7.8×10^{-6}	$\text{Gd}(\text{Pc})_2\text{Ix}$	9.1×10^{-4}
$\text{Ho}(\text{Pc})_2$	6.0×10^{-6}	$\text{Ho}(\text{Pc})_2\text{Ix}$	5.3×10^{-2}
$\text{Er}(\text{Pc})_2$	4.1×10^{-6}	$\text{Er}(\text{Pc})_2\text{Ix}$	3.2×10^{-3}
$\text{Lu}(\text{Pc})_2$	1.8×10^{-5}	$\text{Lu}(\text{Pc})_2\text{Ix}$	-

For the undoped phthalocyanines, the conductivity is related to the size of the lanthanide ion. The order observed is $\text{Pr} < \text{Nd} < \text{Gd} \sim \text{Ho} \sim \text{Er} < \text{Lu}$. This relationship strongly suggests that the overlap between the pi-orbitals between the two macrocyclic units is responsible for the conductivity. This also provides an explanation for the enhanced conductivities of lanthanide phthalocyanines compared with most of their transition metal analogues.

On the average, the conductivity of the iodine-doped phthalocyanines show an increase of four orders of magnitude with respect to the undoped ones. The increase in the electrical conductivity for iodine-doped lanthanide phthalocyanines may be explained by the formation of charge transfer compounds where the phthalocyanine acts as an electron donor.

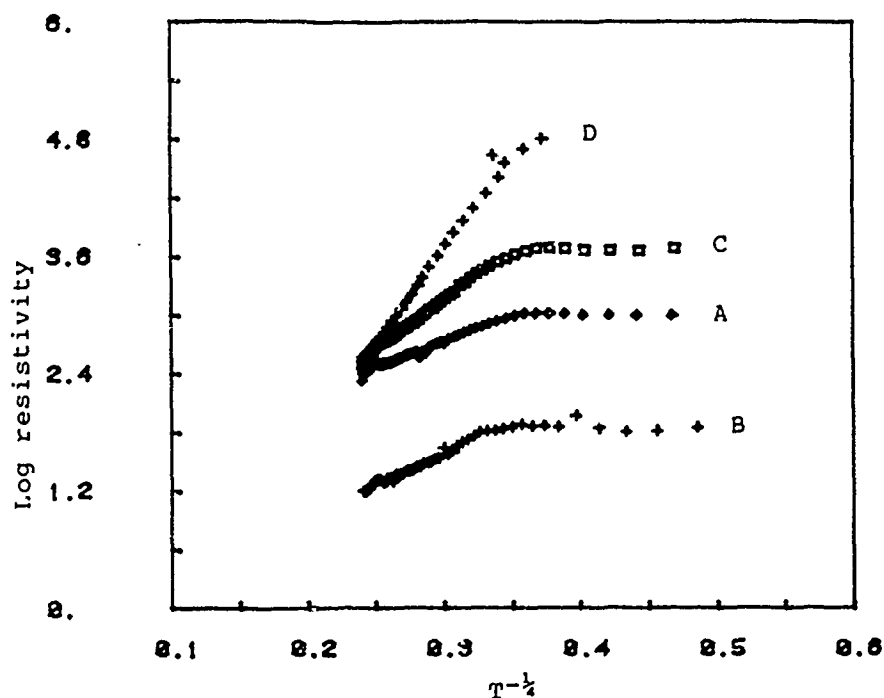


Fig. 1. Logarithm of the resistivity plotted against $T^{-1/4}$ for $\text{Pr}(\text{Pc})_2\text{Ix}$ (A), $\text{Nd}(\text{Pc})_2\text{Ix}$ (B), $\text{Gd}(\text{Pc})_2\text{Ix}$ (C) and $\text{Er}(\text{Pc})_2\text{Ix}$ (D).

In a plot of the $\log(\text{resistivity})$ vs $T^{-1/4}$ (Figure 1), the resistivity increases linearly as the temperature decreases, and then levels off at very low temperatures. This behavior may be explained by a variable-range hopping mechanism for heavily-doped semiconductors [10].

The iodine may be considered as a p-type acceptor that creates a narrow band of acceptor levels. These levels are close to the

top of the valence band, so that the electrons can reach the acceptor level from the valence band at very low temperatures. The iodine content determines the number of acceptor levels and thus the temperature dependance of extrinsic conduction. The greater the percentage of iodine, the wider the temperature interval. The conductivity does not change very much at very low temperatures because the increase in the number of holes created in the valence band is counterbalanced by the decrease in the mean free path of the holes due to phonon scattering.

Since the conductivity measurements were carried out on powders pressed into pellets, the values found are averages that must be considered as a lower limit to the value of a single crystal. We have prepared single crystals of the lanthanide phthalocyanines by electrochemical means; unfortunately, the small size of the crystals has precluded the measurement of their conductivities.

Magnetic results

The-f electrons are responsible for the magnetic properties of the lanthanide phthalocyanines. The magnetic moments at room temperature and the Weiss constants are listed in Table 2.

TABLE 2

Magnetic properties of lanthanide phthalocyanines

Compound	μ -eff (B.M.)	Θ (K)	Compound	μ -eff(B.M.)	Θ (K)
Pr(Pc) ₂	3.7	-111	Pr(Pc) ₂ Ix	2.8	-53
Nd(Pc) ₂	2.8	- 59	Nd(Pc) ₂ Ix	3.8	-34
Gd(Pc) ₂	7.5	6	Gd(Pc) ₂ Ix	7.4	-3.5
Ho(Pc) ₂	10.2	- 2	Ho(Pc) ₂ Ix	12.2	-11
Er(Pc) ₂	8.0	- 4	Er(Pc) ₂ Ix	11.0	-8.8
Lu(Pc) ₂	1.7	-	Lu(Pc) ₂ Ix	1.0	-

The temperature dependance of the magnetic susceptibility follow the Curie-Weiss law through the temperature range studied. The magnetic moments obtained for the iodine-doped compounds differ from those of the undoped complexes, except for gadolinium. Furthermore, the EPR spectra of all the iodine-doped phthalocyanines show a narrow signal with a g-value of 2.00, as

has been observed previously [11]. These magnetic results indicate that partial oxidation with iodine creates an organic free radical which may have an exchange interaction with the f-electrons. Low-temperature susceptibility measurements to confirm these observations are underway.

ACKNOWLEDGEMENT

This work was partially funded by the Office of Naval Research.

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